GAS LAWS IN THE FREE ATMOSPHERE

Meteorology, like Astronomy, is primarily an observational science rather than a laboratory science. This is because the complex mixture of gases, liquids, solids, charged particles, and photons that make up the free atmosphere behaves differently in the free state than when some small portion of it is abstracted, "cleaned up", and subjected to laboratory constraints.

Moreover, many of the gas laws that apply to gases in laboratory containers are not applicable to the gases of the free atmosphere. There are three major reasons why many of these gas laws are generally inapplicable and a host of minor ones.

1. Specific Volume: Firstly, laboratory experiments are carried out in containers of various sizes and shapes; but all these containers have one thing in common. The have a specific volume. This volume is usually symbolized by V in the resulting equations. As a general rule, no gas law requiring a specific volume or equation containing a term denoting a specific volume may be applied to the free atmosphere.

Those of us who study the free atmosphere often refer to "masses" or "parcels" of air. We realize, however, that these entities have no fixed volume or even fixed boundaries. The molecules that make up a mass of air are continually diffusing out of the air mass; while molecules from the surrounding atmosphere are continually diffusing into the air mass. The "volume" of the air mass cannot be assigned any specific numerical value.

2. Holding Variables Constant: The second major reason for the inapplicability of many gas laws to the free atmosphere is that they often require one or more atmospheric variables to be held constant while a second variable is moved or allowed to move over a range of values. This is simply not possible in the free atmosphere. Consequently, no gas law that requires one or more variables to be kept constant may be applied to the free atmosphere.

As a general rule, whenever a mass of air moves across a landscape, all three of the major parameters of the atmosphere (pressure, density, and temperature) can be expected to vary significantly.

3. Conditions of Equilibrium: The third major reason why many gas laws fail in dealing with the realities of a dynamic free atmosphere is that they require that a condition of equilibrium exist—if not actually during the experiment, then at its beginning and at its end. The free atmosphere is—for all intents and purposes—never in a condition of equilibrium. Therefore, laws and equations that require a condition of equilibrium cannot be applied to the dynamic free atmosphere.

If we take any significant portion of the free atmosphere, it is first of all subject to the earth's gravitational field, and secondly involved in rotating about the earth's axis. It is almost certainly being either warmed or cooled. It most likely will be having water vapor added to it or condensing out of it—even if these processes are not visible. Finally, it will probably be in motion relative to the earth's surface. None of these things are compatible with conditions of equilibrium.

The Free and Dynamic Atmosphere: Having gone this far, let us examine some specific gas laws in terms of how they apply or do not apply to atmospheric processes in the free and dynamic atmosphere. Many of these laws are precursors to and are subsumed in the Ideal Gas Equation of State. Consequently, in some cases, I have taken the liberty of paraphrasing them in terms of that equation.

I have also changed the notation to keep it in accordance with the notation used is the rest of these essays. In particular, $\boldsymbol{P}$ and $\boldsymbol{p}$ become $\bar{\boldsymbol{p}}$; and $\boldsymbol{T}$ becomes $\bar{\boldsymbol{T}}$. In both kinetic gas theory and statistical mechanics, it is important to keep in mind that these parameters represent mean values of populations that display a wide range of individual molecular values.

Amonton's Law: Amonton invented a thermometer in the middle 1600's that used the relationships between the temperatures and the pressures of a fixed volume of gas. He found that:

$$\bar{p}_1\bar{T}_2 = \bar{p}_2\bar{T}_1 \text{ (volume kept constant)} \qquad \text{GLF01}$$

Since there was no available temperature scale at that time, his thermometer could not be calibrated for universal use. It is interesting to note, however, that this relationship is a linear one, and therefore implies the existence of absolute zero.

Amonton's Law is **not applicable** to the free atmosphere because it is impossible to maintain a constant volume of the free atmosphere, by definition. If you maintain a constant volume, it is no longer free.

Avogadro's Law: In its simplest form, Avogadro's Law is actually a mathematical identity. It states that a mole of any substance contains exactly the same number of molecules as a mole of any other substance. In this form, it is indisputable, and applies to gases of the free atmosphere as well as to any other gases—whether they are under conditions of equilibrium or conditions of non-equilibrium. The number of molecules in a mole is often referred to as Avogadro's number, and is:

$$N_A = \mathbf{6.02214179 \times 10^{26} \text{ molecules per kilogram-mole}}$$

However, when expressed in terms of the Equilibrium Ideal Gas Equation of State, it is usually put into the form that, **for any given combination of temperature and pressure, the number of molecules per unit volume is the same for any gas or any combination of non-reacting gases under conditions of equilibrium:**

$$\bar{n} = \frac{\bar{p}}{\mathrm{k_B}\bar{T}} \qquad \text{GLF02}$$

Here, $\bar{n}$ is the mean number of molecules per cubic meter, $\bar{p}$ is the mean gas pressure in Pascals, $\mathbf{k_B}$ is Boltzmann's Constant in joules per molecule per degree, and $\bar{T}$ is the mean gas temperature in Kelvins.

Avogadro's Identity is valid only under the same conditions of equilibrium that normally apply to the Ideal Gas Equation of State. Specifically, it is not valid when the air is in net movement—unless, that is, the manometer measuring the pressure is itself drifting with the wind.

<u>The Barometric Formula:</u> This formula assumes that the pressure at elevation ***z*** bears a fixed mathematical relationship to the pressure at base level**.** It is often expressed:

$$\bar{p}_z = \bar{p}_0 \exp - \frac{mgz}{\mathrm{k_B} T} \qquad \text{GLF03}$$

Here, $\bar{p}_z$ is the pressure at elevation z, $\bar{p}_0$ is the pressure at base level, m is the singular molecular mass, g is the gravitational constant, $\mathbf{k_B}$ is Boltzmann's Constant, and T is the singular temperature in Kelvins.

The Barometric Formula is **not applicable** to the free dynamic atmosphere. It assumes that the atmospheric is isothermal from top to bottom, that the mean molecular mass is constant throughout, that the gravitational constant is uniform throughout, that the atmosphere is in a state of equilibrium, and—finally—that the mass of the overlying air is represented by a column, rather than by a conic or pyramidal section. None of these assumptions are true. Moreover, during significant weather events, the distribution of pressure with elevation usually departs radically from this projection.

<u>Bernoulli's Law:</u> Bernoulli showed that **the flow of any fluid (including air) across a surface creates a change in fluid pressure on that surface**. When that flow is parallel to a surface (real or imaginary) the pressure drops in proportion to the square of the fluid velocity. For the atmosphere, the relationship is:

$$\Delta\bar{p} \propto -\tfrac{1}{2}\bar{n}\bar{m}\bar{\varpi}^2 \propto -\tfrac{1}{2}\bar{\rho}\bar{\varpi}^2 \qquad \text{GLF04}$$

Here, $\Delta\bar{p}$ is the change in mean pressure on the surface in Pascals, $\bar{n}$ is the mean number of molecules per cubic meter, $\bar{m}$ is the mean molecular mass in kilograms, $\bar{\rho}$ is the mean mass density in kilograms per cubic meter, and $\bar{\varpi}$ is the wind velocity in meters per second. Note the use of the proportional sign rather than the equal sign. When the direction of flow is not parallel to the sensing surface, other equations must be used, but the principle is the same. Fluid flow produces changes in ambient pressures.

Bernoulli's Law **is applicable** to the free atmosphere, and **must** be applied to understand how ambient atmospheric pressures change in response to changes in wind direction and velocity.

Boyle's/Mariotte's Law: This law may be expressed in a variety of ways. Let's try this one: **If the temperature of a gas is kept constant, then the pressure is inversely proportional to the volume.** Or, mathematically:

$$\bar{p} = \frac{\mathbf{k}}{V} \quad (\bar{T} \text{ kept constant}) \qquad \text{GLF05}$$

Here, $\bar{p}$ is the mean gas pressure in Pascals, V is the total volume in cubic meters, $\bar{T}$ is the mean gas temperature in Kelvins, and **k** is a constant of proportionality.

Boyle's Law is **not applicable** to processes in the free atmosphere because it requires both that the mass of air in the free atmosphere have a specific volume and that the temperature must somehow be maintained at a constant value.

Charles'/Gay-Lussac's Law: This law may be expressed as: **If the pressure of a gas is kept constant, then the volume is inversely proportional to the temperature.**

$$\boldsymbol{V} = \frac{\mathbf{k}}{\overline{\boldsymbol{T}}} \quad (\overline{\boldsymbol{p}} \text{ kept constant}) \qquad \text{GLF06}$$

Here, all the terms retain their previously assigned denotations.

Charles' Law is **not applicable** to processes in the free atmosphere because it requires both that the mass of air in the free atmosphere have a specific volume and that the pressure must somehow be maintained at a constant value. In all fairness, it should be noted that much heating and cooling of parcels of air takes place under conditions that are very close to isobaric. Segregating out a specific volume is another matter.

Dalton's Law of Partial Pressures: This law may be expressed as: **The pressure of a mixture of non-reacting gases is equal to the sum of their individual partial pressures.** That is,

$$\overline{\boldsymbol{p}}_{abc} = \overline{\boldsymbol{p}}_a + \overline{\boldsymbol{p}}_b + \overline{\boldsymbol{p}}_c \qquad \text{GLF07}$$

An interesting logical consequence of this law is that, in essence, every non-reacting gas behaves as if no other gas were present.

Dalton's Law of Partial Pressure **is applicable** to the free atmosphere as long, and only as long, as the air is not moving with respect to the manometer.

Graham's Law of Diffusion: Graham found that **the rate at which gases diffuse is proportional to the square-root of their molecular masses.** Since the kinetic energy of translation is the product of the mass and the mean square of the component velocities, it would appear that some measure of molecular velocity is actually at work. A moment's thought leads us to conclude that this rate of diffusion is a function of the mean velocity at which gas molecules pass through a plane surface. That velocity is the mean impulse velocity:

$$\bar{v}_i = \left(\frac{\pi \mathrm{k_B} \bar{T}}{2\bar{m}_i}\right)^{\frac{1}{2}} \qquad \text{GLF08}$$

Here, $\bar{v}_i$ is the mean velocity normal to the plane of that selected set of molecules actually passing through the plane in some measure of time, $\mathbf{k_B}$ is Boltzmann's Constant, $\bar{T}$ is the mean molecular temperature, and $\bar{m}_i$ is the mean molecular impulse mass of that subset of molecules (See ***Molecular Masses***).

Graham's Law **is applicable** to the free atmosphere when it is still; and **is not applicable** when the air is in motion. Under the latter conditions, turbulent mixing far overwhelms simple diffusion.

Ideal Gas Equilibrium Equation of State (Laboratory Version): This equation relates the parameters of an ideal gas under conditions of equilibrium. Indeed, an Ideal Gas is defined as one that is completely described by the Equation of State under conditions of equilibrium.

$$\bar{p}V = R\bar{T} \qquad \text{GLF09}$$

Here, $\bar{p}$ is the pressure in Pascals, V is the volume of one mole of the gas in cubic meters, **R** is the universal gas constant in joules per mole, and $\bar{T}$ is the absolute temperature in Kelvins.

The term **R** is actually Avogadro's Number times Boltzmann's Constant. Consequently it has the value:

$$\mathbf{R} = 8.314447 \times 10^3 \text{ Joules per kg-mole per Kelvin}$$

This version of the *Ideal Gas Equation of State* is **not applicable** to processes in the free atmosphere because it requires both that the mass of air in the free atmosphere have a specific volume and that the number of molecules in the mass of air is somehow maintained at a constant value.

Ideal Gas Equilibrium Equation of State (Kinetic Gas Version): In kinetic gas theory, the *Ideal Gas Equation of Stat*e is often expressed as:

$$\bar{\boldsymbol{p}} = \bar{\boldsymbol{n}} \mathrm{k_B} \bar{\boldsymbol{T}} \qquad \text{GLF10}$$

Here, $\bar{\boldsymbol{p}}$ is the mean gas pressure in Pascals, $\bar{\boldsymbol{n}}$ is the mean number of gas molecules per cubic meter, $\mathbf{k_B}$ is Boltzmann's Constant in joules per molecule per degree, and $\bar{\boldsymbol{T}}$ is the mean molecular temperature in Kelvins. (See ***The Nature of Atmospheric Pressures*** for the derivation of this equation.)

This version of the *Ideal Gas Equation of State* is **not applicable** to parcels of air in motion or anytime weather is occurring.

Ideal Gas Equilibrium Equation of State (Statistical Mechanical Version): In statistical mechanics, under conditions of equilibrium, the *Ideal Gas Equation of State* may be expressed as:

$$\bar{\boldsymbol{p}} = \bar{\boldsymbol{n}} \bar{\boldsymbol{m}}_i \boldsymbol{\sigma}^2 \qquad \text{GLF11}$$

Here, $\bar{\boldsymbol{p}}$ is the mean gas pressure in Pascals, $\bar{\boldsymbol{n}}$ is the mean number of molecules per cubic meter, $\bar{\boldsymbol{m}}_i$ is the mean molecular impulse mass in kilograms, and $\boldsymbol{\sigma}^2$ is the mean of the squares of the axial molecular velocities.

This version of the *Ideal Gas Equation of State* is **not applicable** to parcels of air in motion or anytime weather is occurring.

Maxwell-Boltzmann Distribution: This is a distribution of molecular velocities in an ideal gas that was first developed by Maxwell and later generalized by Boltzmann. For our purposes, we will express it in terms of $\boldsymbol{\sigma}$, the square-root of the mean of the squares of the individual velocities. In a statistical sense, this term is also the standard deviation, since the mean value of the distribution is zero.

$$\boldsymbol{\sigma}_x = \left(\frac{1}{N} \sum_{1}^{N} v_x^2 \right)^{\frac{1}{2}} \qquad \text{GLF12}$$

Here, $\boldsymbol{\sigma}_x$ is the root-mean-square velocity along the x-axis, N is the number of molecules involved, and $\boldsymbol{v}_x$ is any individual molecular velocity along the x-axis. Since, under conditions of equilibrium, the distribution of molecular velocities is the same in every conceivable direction, we may drop the subscript and simply refer to $\boldsymbol{\sigma}$.

The probability of a molecule having some particular velocity $\boldsymbol{v}$ over a single axis of movement can be expressed by the normalized version of the ***probability density curve***:

$$\Phi(v) = \frac{1}{\sigma^3} \sqrt{\tfrac{2}{\pi}}\, v^2 \exp - \frac{v^2}{2\sigma^2} \qquad \text{GLF13}$$

Here, $\Phi(v)$ is the probability that a molecule chosen at random will have velocity $\boldsymbol{v}$, and all the other terms have their agreed meanings.

The Maxwell-Boltzmann distribution **is applicable** to the free atmosphere whenever the air is either isothermal or changing its temperature in a uniform fashion (such as occurs during adiabatic processes or during radiative heating and cooling).

Van der Waal's Equation: This last of the major gas laws to be discovered postulates that **at low temperatures and high densities, forces exist between molecules that both attract and repel them**. This is usually expressed as:

$$\left(\bar{p} + \frac{a}{V^2} \right)(V - b) = R\bar{T} \qquad \text{GLF14}$$

Here, $\boldsymbol{a}$ and $\boldsymbol{b}$ are coefficients that vary with the nature of the gas, and the other terms have their previously defined meanings. At normally-occurring temperatures and pressures, $\boldsymbol{a}$ and $\boldsymbol{b}$ approach zero, and the equation becomes:

$$\boldsymbol{\bar{p}V = R\bar{T}} \qquad \text{GLF09}$$

the *Ideal Gas Equilibrium Equation of State*.

Van der Waal's Equation **is valid for the free atmosphere**, and becomes particularly applicable when dealing with evaporation and condensation phenomena.

REFERENCES

INTERNAL REFERENCES: These are other papers in this collection that are either cited or linked during the course of the discussion or whose content is especially relevant to the current discussion.

The Dynamic Atmosphere – This paper emphasizes the atmosphere's mutability.

The Kinetic Theory of Gases – This is a brief introduction to the concept that atmospheric gases are composed of very large number of very small molecules moving in a variety of directions with a known distribution of speeds.

Statistical Mechanics – This is a brief introduction to the uses of probability theory to predict the mean parameters of large collections.

The Ideal Gas – This is a brief introduction to the concept of an ideal gas with an emphasis on how such ideal gases differ from real gases.

The Nature of Atmospheric Pressures – This paper defines gas pressures ($\bar{p}$) in terms of kinetic gas theory and statistical mechanics. The Universal Pressure Equation is introduced.

Molecular Masses – This paper defines the molecular mass parameters ($\bar{m}, \bar{m}_i$) and shows how their values were calculated.

The Probability Density Curve – This paper discusses the significance and history of the probability density curve. It goes on to show how in its normalized form it is also the distribution function for axial velocities.

<u>EXTERNAL REFERENCES</u>: These are papers by other authors that contain statements or data that are specifically incorporated into the current discussion.

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Walter Benenson, John W. Harris, Horst Stocker, Holger Lutz, editors; **<u>Handbook of Physics</u>**; Springer, New York, 2006.

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Dwight E. Gray; **<u>American Institute of Physics Handbook</u>**; Third Edition, McGraw-Hill, New York, 1972.

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Computational System: All calculations were carried out by Microsoft's© Excel Program 2003 (SP3). The reader should be alerted to the fact that this computational system uses fifteen significant figures for all calculations—whether or not such precision is warranted by the accuracy of the data.